

DEVELOPMENT OF LOW-COST HYDROGEN SENSORS

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Abstract

We describe ongoing research aimed at understanding and improving the speed and reproducibility of our resistive hydrogen sensor, along with complementary efforts in manufacturability and further design improvements. Maskworks were designed to allow for the printing and firing of multi-sensor layouts (15 per substrate) and a large batch of these sensors was produced using standard thick-film manufacturing lines. Piece-to-piece variations of both the as-made resistance and the response of these sensors to hydrogen were within acceptable tolerances, and the sensor design has now been released for commercial prototyping. Automated testing has begun in order to develop long-term performance data. Dynamic response of selected sensors was measured before and after exposures to methane, hydrogen sulfide, and carbon monoxide, in order to assess the effects of interference gases and surface poisoning. As expected, H_2S degrades the sensor somewhat, whereas CH_4 and CO do not create significant interference when air is present.

Introduction

The goal of the program is to develop rugged, reliable, and cost-effective thick-film resistive sensors in order to encourage widespread use within a developing National hydrogen infrastructure. This project supports that goal by continuing the development

of optimized materials and designs while maintaining good manufacturability by conventional processes. Performance testing under cyclic conditions provides data on speed and sensitivity that will define appropriate applications and guide the engineering design of sensor packages and electronics. Also, understanding issues associated with cross-sensitivity, contamination, and poisoning will help us to develop strategies to mitigate these effects and improve sensor reliability and lifetime.

Our resistive hydrogen sensor (Hoffheins 1995) was designed for conventional thick-film manufacturing techniques. The sensor uses four Pd-containing resistors in a Wheatstone bridge arrangement. Two of the resistors are exposed to the atmosphere and when hydrogen is present, H_2 dissociates on the surfaces of these uncovered Pd resistors and atomic H diffuses into the Pd. The resulting increase in the electrical resistance of the Pd (Lewis 1967, Barton 1963) is measured by the shift in the bridge voltage. The other two Pd resistors are covered by a dense hermetic dielectric film, thereby forming reference resistors to eliminate the effect of temperature fluctuations (the temperature coefficient of resistivity of Pd is $\sim 3 \times 10^{-3}/^{\circ}C$).

The sensor is fabricated by screen printing three distinct materials on an alumina substrate. The Pd resistors are DuPont Conductor Composition 12345-67A fired at $1000^{\circ}C$; solderable pads at the junction points are DuPont Conductor Composition 4093 fired at $900^{\circ}C$; the hermetic passivation layer covering the reference Pd resistors is DuPont Dielectric Composition 5704 fired at $850^{\circ}C$. All firings are done in air using the manufacturer's recommended temperature profile.

Experimental Activities

Manufacturing Scaleup and Evaluation

During the early stages of development, experimental sensors were made by printing them individually on standard 1" x 1" substrates, using a small benchtop screen printer. These samples were adequate for evaluating the basic design, but the next step toward a commercially viable product was to make a large number of identical sensors, using commercial equipment, for statistical evaluation and long-term testing. A prototype batch was fabricated at DuPont (Research Triangle Park, NC) using perforated substrates designed to accommodate 15 sensors, which are snapped apart after firing (Figure 1). An initial run of 420 sensors was made using this setup. The Pd metallizations were 10 mil wide with 10 mil spacing, giving each of the four resistors a nominal resistance of ~ 100 ohms. Profilometry data on the fired sensors indicated the average film thickness of the Pd metallization was about 4-6 μm .

Characterization and testing of these sensors included analysis of the piece-to-piece variation in as-fired resistances of the individual resistors. The bridge resistances showed better than $\pm 5\%$ repeatability of resistances within a substrate and among substrates. The consistency is more than adequate. Limited testing of sensors exposed to hydrogen shows consistent response from sensor to sensor.

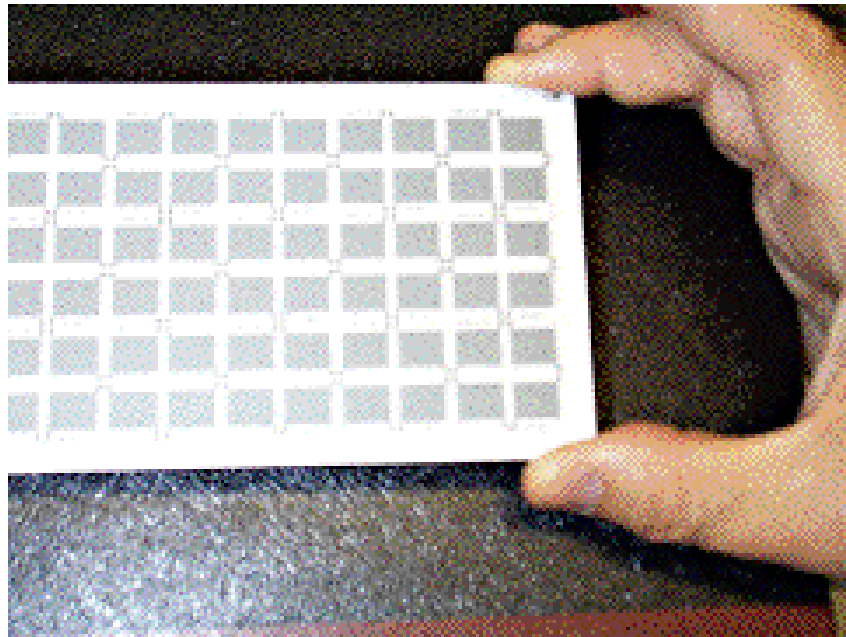


Figure 1 - Multiple Sensor Layout, 15 per Substrate

Based on the good reproducibility of the multisensor layout, a prototype design has been released for a short commercial manufacturing run. This new design uses 7.5 mil lines at 7.5 mil spacing. The bridge circuit is 1/2" x 1/2" and will be fabricated on a 1/2" x 1" substrate, with some additional electronics (including temperature sensing circuitry) fabricated on the other half of the substrate.

Development of More Rugged Designs

In previous work, sensors exposed to very harsh conditions (up to 30% hydrogen at temperatures up to 200°C) exhibited severe delamination of the exposed Pd metallization from the substrate as shown in Figure 2. We have begun to explore two alternate methods (U. S. Patent Pending) for mitigating this effect with minimal added cost.

The first approach is to extend the pattern of the passivation layer so that it completely covers the reference Pd resistors and also extends in thin bands, crossing the sensing resistors at selected points, Figure 3. This is intended to help hold them down to the substrate while leaving most of their area exposed to the atmosphere. The advantage of this approach is that it requires only a modification of the maskwork, with no added printing or firing steps.

The second approach is to completely cover the sensing resistors with a dielectric layer that is substantially continuous but porous enough that the underlying metallization is accessible to the atmosphere. This layer must obviously be different from the hydrogen-impermeable layer covering the reference resistors, so one more print step is added;

however, the porous dielectric can be formulated to be cofirable with the dense dielectric so that no added firing step is needed. To test this idea, we added 10, 20, and 30%

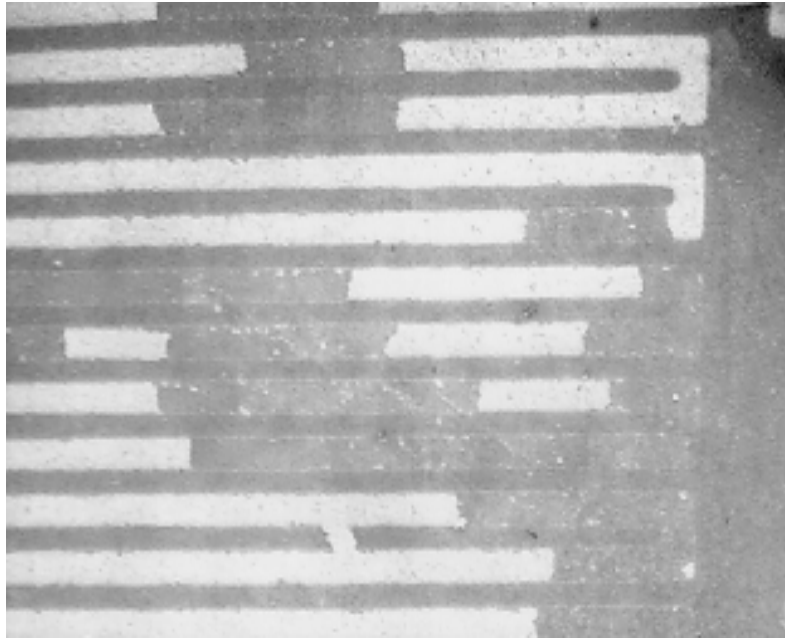


Figure 2 - Failure of Pd Metallization Under Harsh Conditions

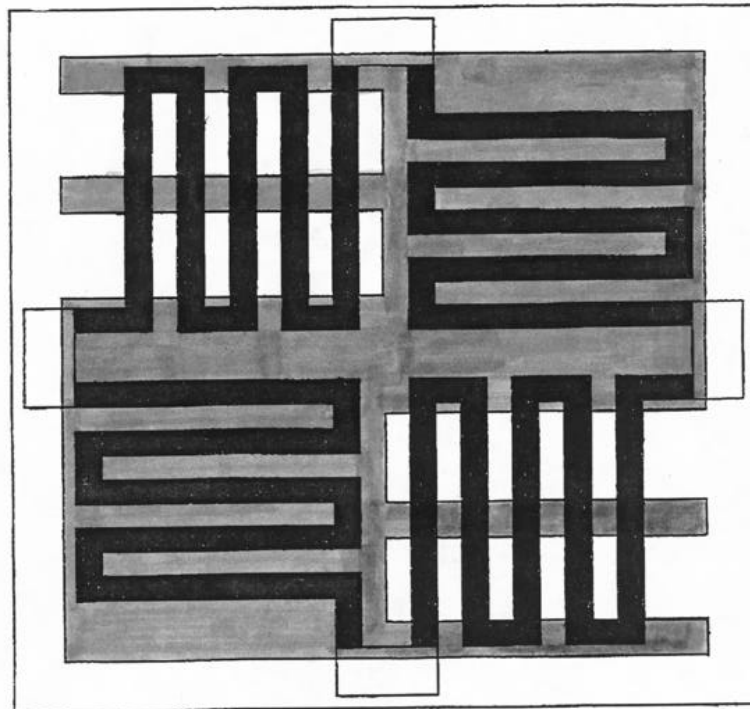
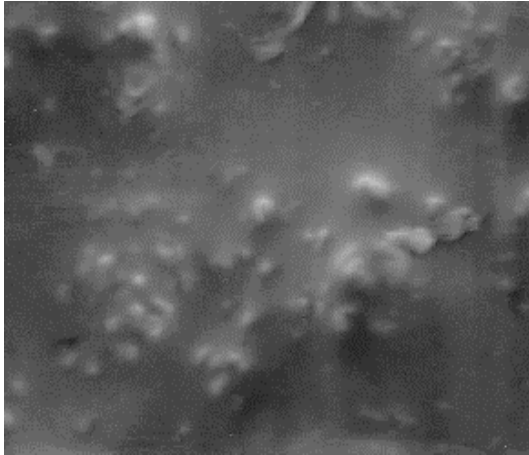
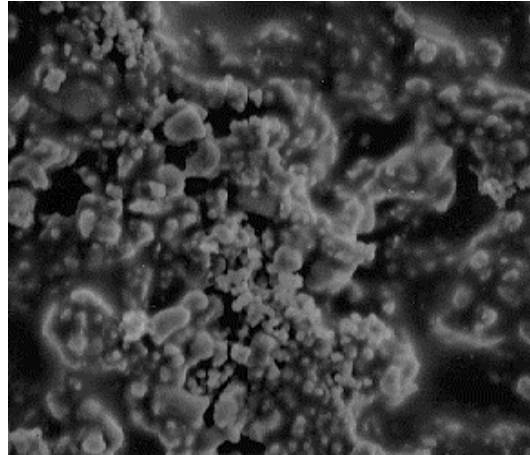


Figure 3 - Modified Sensor Design with Added Support Structures

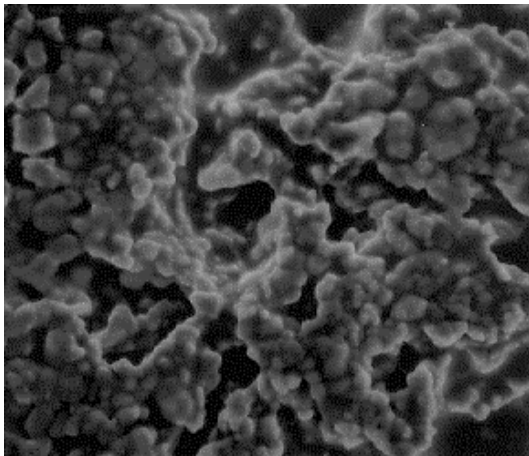
alumina powder (Baikowski CR-6) to the DuPont 5704 dielectric composition, thinning as needed with DuPont 8672 thinner. These materials were printed onto bare alumina substrates and fired at 850°C in air. The fired layers adhered well to the substrates, and as expected they had significant porosity, which increased with increasing alumina content as shown in Figure 4. Current plans call for fabricating some sensors using these modified designs and materials, and determining the effect of the added structures on response time.



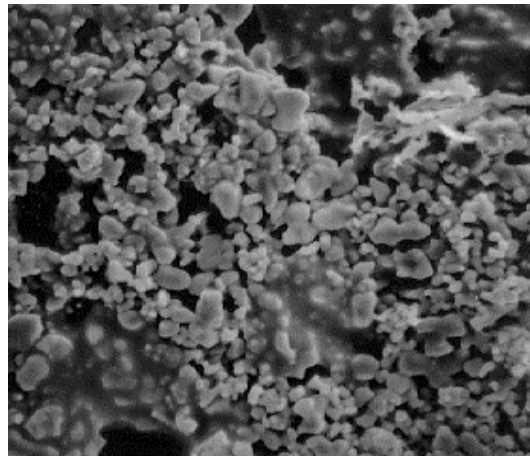
5704



5704 + 20% Al₂O₃



5704 + 10% Al₂O₃



5704 + 30% Al₂O₃

Figure 4 - Fired Dielectric with Alumina Additions (SEM 10,000X)

Testing and Characterization

Two types of testing have been started: Life testing and repeatability testing. Prior to use, the sensors must be “awakened”. These processes and results are summarized below.

The wake-up procedure is to expose a sensor to a gas mixture of 4% hydrogen and 96% argon for an hour. Prior to wake-up, a sensor will not respond to hydrogen. The wake-up process reduces a deep oxide layer that is picked up during manufacture (the firing process).

Awakened sensors were first exposed to some limited life testing. The test equipment periodically and automatically exposes groups of sensors to different levels of hydrogen. The levels are 0%, 0.4%, and 2%. The balance of the gas is dry air. Three channels, each with different exposure periodicity, are used. Initially, a group of sensors are exposed every four hours, 24 hours a day, for a week. If the sensors are stable after that period, then they are moved to a second channel in which they are exposed once a week for a month. Then they are moved to the third channel that exposes them only once a month. The sensors will stay in the latter channel for at least a year. To date, an initial batch of sensors have passed channels one and two and are in the third channel. The responses of the sensors are stable.

All working gas sensors must be able to accommodate various impurities and interference gases that will always be present in the environment. Knowing the effects of likely interference gases (especially organics, CO, and moisture) and surface poisons (particularly sulfur) will allow us to understand and predict how the sensors will behave in real applications and to design protective strategies when needed. Dynamic response of selected sensors (to 2% hydrogen) was measured before and after exposures to CH₄, H₂S, and CO, in order to assess the effects of these species.

The response of a sensor to 2% hydrogen, before and after exposure to 10 ppm H₂S (in nitrogen), Figure 5, shows that H₂S degrades the sensor. The observed slowing of the dynamic response does not recover with subsequent exposures to either air or hydrogen. We attribute this to irreversible poisoning of the catalytic properties of the Pd surface by sulfur.

The dynamic response to 2% H₂ for a sensor as received, after 1 hr in air, and after 1 hr in 100 ppm CH₄ (in nitrogen) is shown in Figure 6. It can be seen that CH₄ has no significant effect on rise time in 2% H₂.

Figure 7 shows the response of the sensor in the as-received condition and after a 1 minute exposure to a high concentration of CO, after which the rise time in 2% H₂ went from less than a minute to about four minutes. Following a brief exposure to air (at about 6 minutes into the run), the dynamic response to H₂ returned to its original behavior. We attribute these results to high surface coverage of CO on the Pd, which slows the uptake of hydrogen but does not prevent it from ultimately reaching its equilibrium value. A brief exposure to air removes the CO, possibly by oxidizing some of it to CO₂, after which the original rise time of the sensor is restored. (A similar, but somewhat less dramatic effect is seen after a purge with nitrogen, suggesting that adsorbed CO is fairly readily removed from the Pd surface.) This implies that for a safety monitor intended to detect concentrations of H₂ in air, reasonable concentrations of CO will not interfere or slow the response.

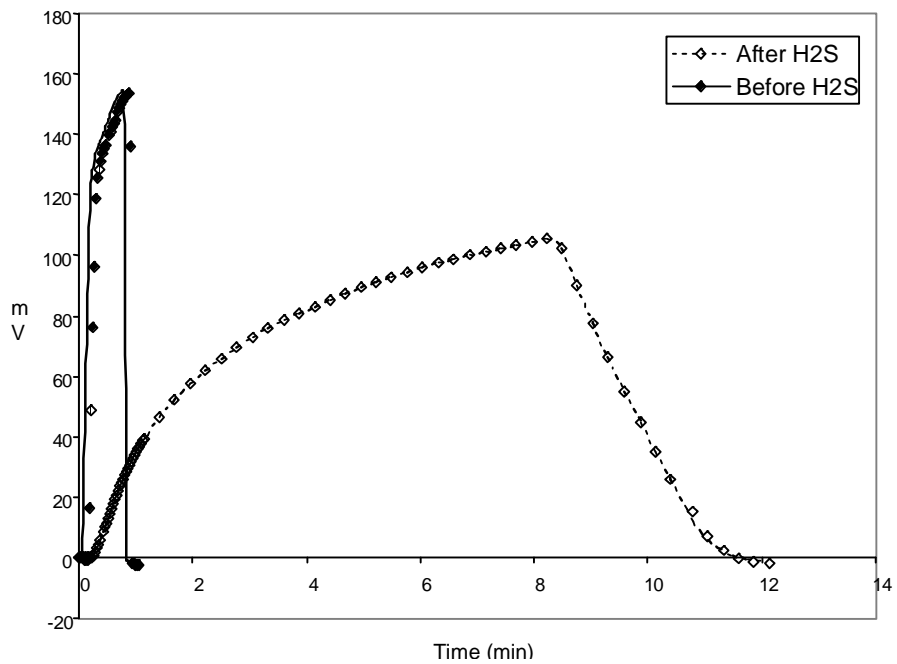


Figure 5 – Response to 2% H₂ Before and After Exposure to 10 ppm H₂S

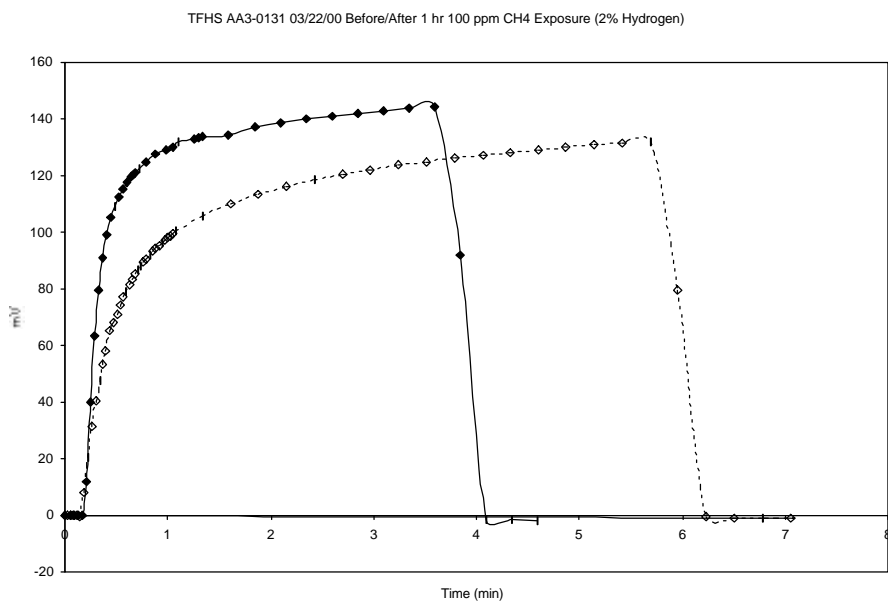


Figure 6 – Response Before and After Exposure to 100 ppm CH₄

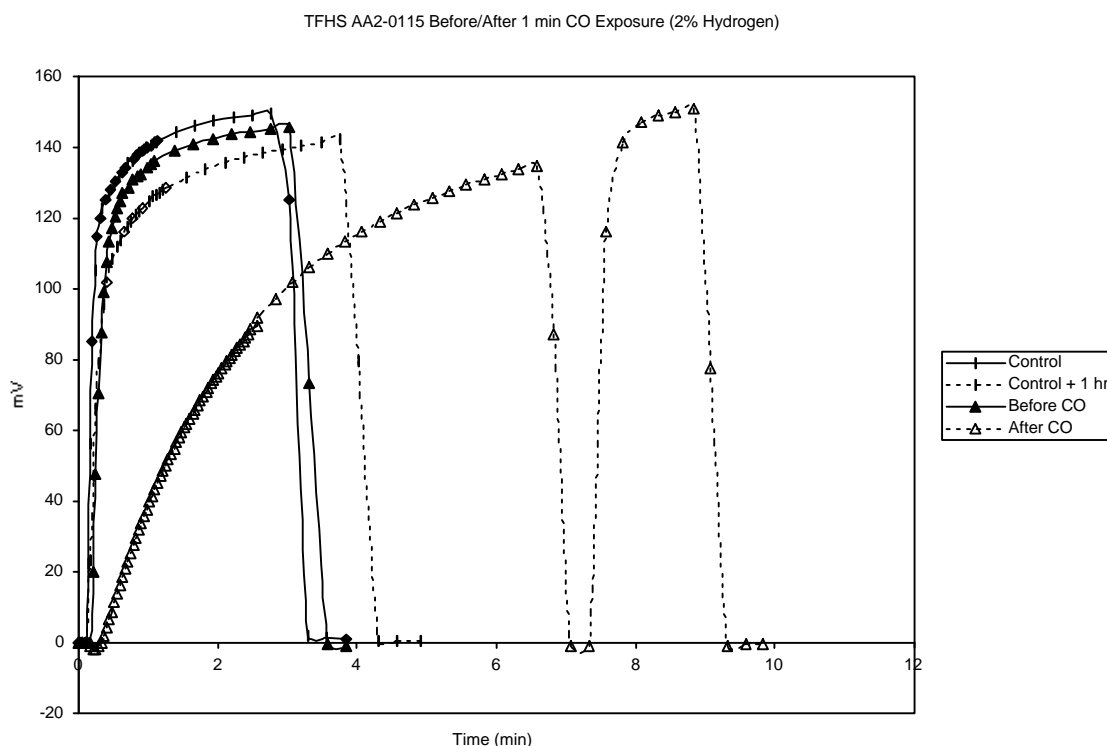


Figure 7 – Response After Exposure to CO and After 1 min in Air

SEM analysis was done on selected samples before and after exposures. XPS analysis on the as-fired sensor detected an oxygen-rich layer, as well as significant amounts of carbon, much of which was removed by the "wake-up" process. This indicates that the hydrogen may be performing a cleaning mechanism on the Pd surface (and would also explain the cyclic testing data in which we observed that the response time only degrades after a prolonged period without hydrogen exposure). The SEM photographs themselves reveal a subtle change in morphology, notably an edge rounding effect that is most likely due to the volume expansion of the Pd after H absorption. The change in specular properties has also been attributed to this expansion (J. R. Pitts, personal communication), although the removal of a native palladium oxide layer could also play a role in the color change (dark gray to silver) observed upon first exposure to H₂.

Market Analysis and Commercialization

DCH Technology continues to conduct economic analyses in collaboration with end users in several fields.

- For the automotive market, low cost is important as well as rapid response. Strategies are being developed for heating the sensor in order to help meet performance specifications that include very low ambient temperatures. It is important to

emphasize that the automotive industry needs a significantly faster response. To provide this, with any Pd-based hydrogen sensor, the dynamics of the surface under exposure must be understood. This is not just a good thing to do; it is necessary and if this isn't done, the Nation will not have an acceptable sensor for hydrogen cars.

- For personal safety monitors (badge) or distributed area sensors (wireless) DCH has designed appropriate electronics and packaging for battery-powered applications. Second-generation electronics are in conceptual design.
- For battery boxes, long-term reliability is a key performance attribute because of limited accessibility of many installations. DCH will institute alpha testing with battery box customers using “badge” electronics.

Conclusions

1. The thick-film hydrogen sensor is inherently manufacturable by standard processes. Sensors made on standard production equipment using multiple-sensor layout (15 per substrate) are uniform and reproducible.
2. Rise time of the sensor output (in response to 2% hydrogen) is less than 1 minute at ambient temperature.
3. Carbon monoxide slows the response in the absence of air, but in the presence of air CO does not appear to have an effect on response time. Methane has no significant effect on response to hydrogen.
4. Hydrogen sulfide greatly degrades the performance of the sensor, most notably by increasing the response time. This is attributed to poisoning of the surface catalytic properties of the Pd by sulfur.

Future Work

All hydrogen-specific sensors that rely on the unique properties of Pd share many issues in common. Among these are:

- Chemisorbed oxygen or the formation of a PdO film on the surface after long times in ambient air can slow the response when hydrogen is first encountered.
- The processes that occur during first exposure to hydrogen are sensitive to small changes in the catalytic properties of the Pd surface. The role of processing variables, contaminants, etc. must be better understood.
- Mechanical stability of the films will be influenced by volumetric changes during repeated exposures to moderate hydrogen concentrations or during a single exposure to a high concentration of hydrogen.
- Kinetics of hydride formation and decomposition will affect the observed time constants whenever hydrogen concentrations are high enough to create small amounts of hydride phases.

Our plan is to continue our scientific studies of the foregoing issues in support of the ongoing commercialization activities at DCH Technology. Specifically, we plan to conduct *in situ* X-ray diffraction on the sensors, during exposures to various concentrations of hydrogen at various temperatures. This will help to elucidate the degree to which hydride formation occurs, its effect on stresses in the Pd film, and the speed with which the hydride decomposes. We also hope to study the existence of surface oxides and their removal during hydrogen exposures. Last, we plan to continue surface analyses of samples after exposure to interference gases, contaminants, and poisons.

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